

Abstract

Surface diffusion of CO adsorbed on Pt nanoparticle catalysts was measured in solid/liquid interface at and near room temperature, 253 K – 293K, by using electrochemical nuclear magnetic resonance (EC-NMR) spectroscopy with a spin labeling pulse sequence. ^2H NMR indicates that the electrolyte remains in a liquid-like state at temperatures where the experiments were performed. The presence of electrolyte considerably impedes the surface diffusion of CO as compared to that under ultrahigh vacuum (UHV) or gas phase conditions. For fully CO covered sample, exchange between different CO populations, driven by a chemical potential gradient, is suggested as the main mechanism for CO diffusion. For partially CO covered samples, diffusion parameters, activation energies (E_d) and pre-exponential factors (D^0) show CO coverage dependence. E_d decreases linearly with increasing CO coverage. This indicates that the CO-CO repulsive interactions make a stronger influence on the coverage dependence of the activation energy than does the nature of the CO adlayer structure. Pre-exponential factor, D^0 , shows an exponential decrease as CO coverage increases. This exponential decrease can be explained with free site hopping as the main mechanism for CO surface diffusion at partial coverages. Diffusion measurement was also carried out for CO adsorbed on small carbon supported Pt nanoparticles. For full and partial covered samples, diffusion coefficients (D_{CO}) show size dependence. That is, for CO adsorbed on small Pt nanoparticles, the diffusion is slower as compared to CO on large Pt nanoparticles. However, root mean square displacement values, calculated from diffusion coefficients, show that CO motion is fast enough to cover the whole particle in 1s. Properties of CO on Ru and Rh were studied by using ^{13}C NMR for better understanding their role in Pt based catalysts. ^{13}C NMR spectra of CO adsorbed on Ru and Rh nanoparticle show a symmetrically broadened peak having a large isotropic shift as compared to CO adsorbed on supported Ru and

Rh catalysts. CO adsorbed on Ru was metallic and motional narrowing of the spectrum and deviation from Korringa behavior indicate rapid CO surface diffusion. Fermi level local density of states for CO 5σ and $2\pi^*$ shows that the CO adsorption bond is weaker on Ru than on Pt. For Full coverage, diffusion coefficient of CO adsorbed on Rh is similar to that for CO on Pt as observed under UHV condition. ^{195}Pt NMR spectra of three carbon supported Pt nanoparticles whose size is 1.6, 2.6, and 4.8 nm in average diameter show size dependence. Although the variation in the NMR spectra with different particle size can be explained as due to the effect of the layer by layer variation of the s-type and d-type local density of states, difference in the surface electronic properties of these Pt/C catalysts due to size variations was negligible.